Perfumer's notes

Javanol

Fragrance creation with sandalwood oil substitutes

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The growing scarcity—and resulting increased price—of sandalwood oil explains the fragrance industry's continuous search for synthetic substitutes. Javanol (Givaudan), prepared from naturally occurring α-pinene, represents a new tool in terms of performance and naturalness of scent.

Sandalwood Oil

Sandalwood oil is one of the most precious and widely used raw materials in perfumery.[1] Extracted from the heartwood and roots of *Santalum album* trees grown in India and Indonesia, the oil has played an important social, cultural, religious, medical and aesthetic role for millennia. In perfumery, it is valued not only for its multifaceted woody, creamy, sweet, warm and animalic natural scent, but also for its outstanding fixative and blending properties.

Sandalwood trees, which are semi-parasitic evergreens, need particular climate and light conditions in order to thrive. Because of the absence of heartwood in young trees, they should not be harvested for at least 20–25 years, at which point their heartwood is separated, transformed into powder and steam distilled to produce the precious oil. This long period of growth (optimally 30–50 years), combined with the declining population of the species (due mainly to continual deforestation, smuggling and the devastating spike disease), have resulted in the dwindling availability of a good quality sandalwood oil, causing prices to soar. After a spectacular price increase in 1974 and a period of fluctuating moderate growth, the cost of sandalwood oil again is increasing rapidly. From $40/kg in 1973, sandalwood oil prices climbed to $210/kg a year later, then dropped back to $140/kg in 1992. Today, the material is priced at around $1,400/kg. Strict regulations imposed on the sandalwood trade by the Indian and Indonesian states and attempts to enlarge the geographic area of *S. album* plantations to Australia—home to another sandalwood species, *Santalum spicatum*[a]—have had a limited effect on the general trend. In perfumery today, the use of natural sandalwood oil is restricted almost exclusively to fine fragrances.

Synthetic Substitutes

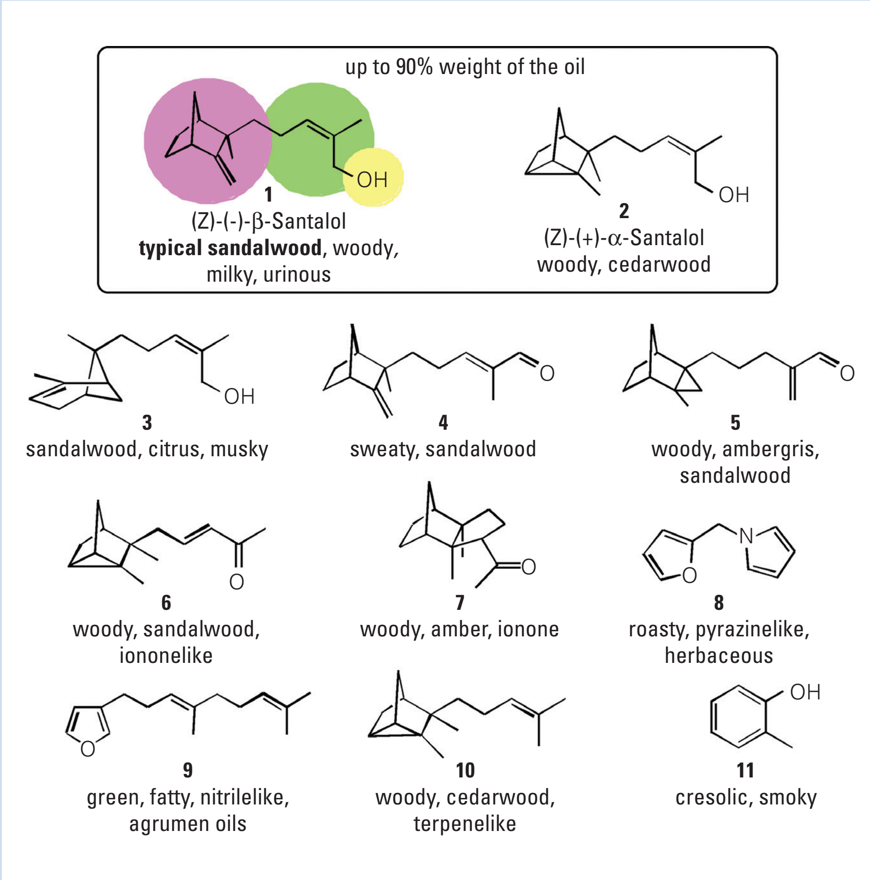
Sandalwood oil is comprised of more than 100 odorant compounds. Their contribution to the complex olfactory profile of sandalwood oil has been the subject of extensive research and controversy for decades.[1b,2] Anyone contemplating the structures of the main olfactory constituents of sandalwood oil (two alcohols **1** and **2**, representing about 90% of its weight, and an impressive series of other alcohols, ketones, aldehydes, acids, phenols, heterocycles and hydrocarbons in more or less trace amounts; F-1) obviously will conclude that the full spectrum of this exquisite scent cannot be reproduced by a single molecule. Therefore, replicating the material as closely as possible still represents an exciting challenge.

The first sandalwood oil substitutes appeared even before the unavoidable shortages of this raw material became evident[1b,3] In the late 1930s, a serendipitous finding gave rise to sandalwood-smelling mixtures of terpenylcyclohexanols **12** (F-2).[4] Interestingly, the

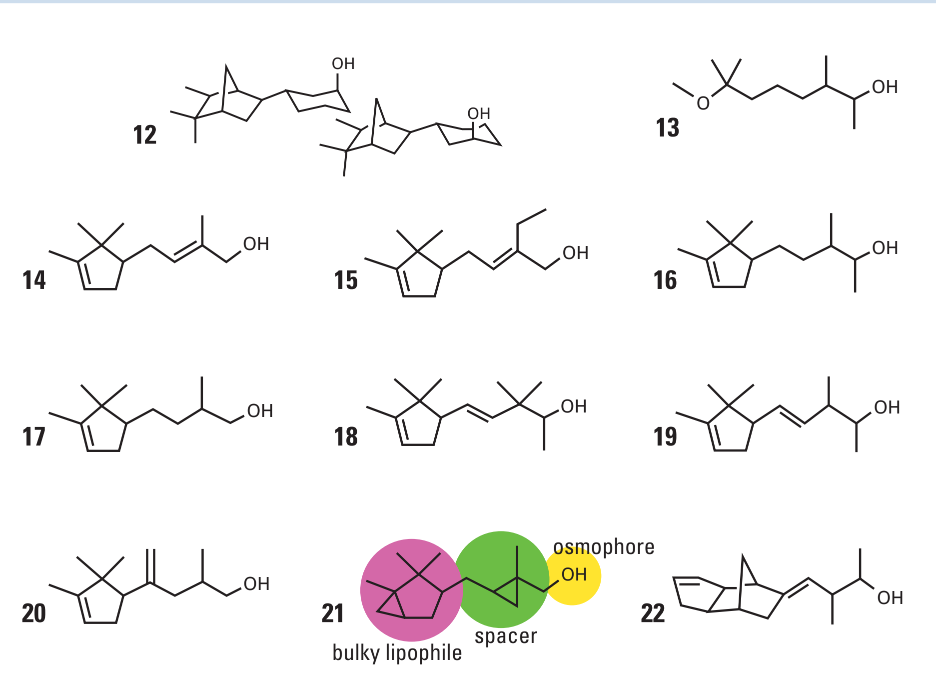
[a] *Santalum spicatum* oil is less valued than sandalwood oils from East India and the Indonesian islands.

relative configurations of their main olfactory constituents were not established until relatively recently (1969); the absolute configurations were published only in 1997. Due to the vicissitudes of World War II, these mixtures were not introduced to the market until 1960, first under the name of Sandela (Givaudan). This was the age when synthetics were changing modern perfumery. Followed by many generics, Sandela continues to constitute an inexpensive and efficient replacement of sandalwood oil, even today. Osyrol (Bush Boake Allen, now IFF) (**13**), launched in 1973, marked the next milestone in the history of sandalwood oil mimics. The real breakthrough finally came with the derivatives of α-campholenic aldehyde (**24**). Odor descriptions of the first members of this family (**14** and **15**), patented in East Germany in 1968, were somewhat misleading: "resembling musk and sandalwood."[5] In reality, these materials' main olfactory filiation was sandalwood. The entire armada of close analogues of **14** and **15** and their copies today account for the best and most often used synthetic substitutes of sandalwood oil.[6]

Selected main olfactory constituents of sandalwood oils (for structural diversity; other alcohols, aldehydes and ketones similar to 1–7 were omitted for clarity). **F-1**



Synthetic sandalwood odorants **F-2**



12 Sandela (Givaudan), Sandel (H&R, now Symrise), Sandiff (IFF), Santalydol, Santalex (Takasago)

13 Osyrol, (BBA, now IFF)

14 Madrol (Dragoco, now Symrise), Mysosan, Sandafleur, Sandalmysore Core (Kao), Sandelice (Cognis), Santalinol, Santalaire, Santaliff (IFF)

15 Bacdanol (IFF), Balinol, Bangalol (Quest), Chandanol, Dartanol, Levosandol (Takasago), Radjanol (Givaudan), Sandanol, Sandol, Sandolene, Sandranol (Dragoco, now Symrise), Sanjinol (IFF)

16 Sandalore (Givaudan), Sanflore

17 Brahmanol (Dragoco, now Symrise)

18 Polysantol (Firmenich), Supersantol

19 Ebanol (Givaudan)

20 Firsantol (Firmenich)

21 Javanol (Givaudan)

22 Fleursandol (Symrise)

Discovery of Javanol

The steady improvement of the initial templates—from Sandalore (Givaudan) (**16**) to Polysantol (Firmenich) (**18**) to Ebanol (Givaudan) (**19**)—was accompanied by numerous attempts to make the rational design of new odorants a reality.[2b,6a,7] The research on the mechanisms of olfaction—rewarded by the 2004 Nobel Prize attributed to R. Axel and L. Buck—continues to reveal the unanticipated complexity of the whole odor perception process.[8] According to the proved paradigm of combinatorial receptor codes for odors, the scent of a molecule is due to a combination of interactions between the molecule and odorant receptors of different types.[8] This may imply that more than one electronic shape of an odorant is necessary to trigger a given odor sensation. Undeterred by this additional difficulty, fragrance chemists keep trying to define the electronic shape(s) of molecules capable of eliciting a genuine sandalwood oil scent. This shape has been decomposed into three structural features: the so-called osmophoric polar hydroxyl group linked by a spacer to a bulky, lipophilic moiety. They are easily identifiable in **1**, **2** and all the substitutes depicted in F-2.

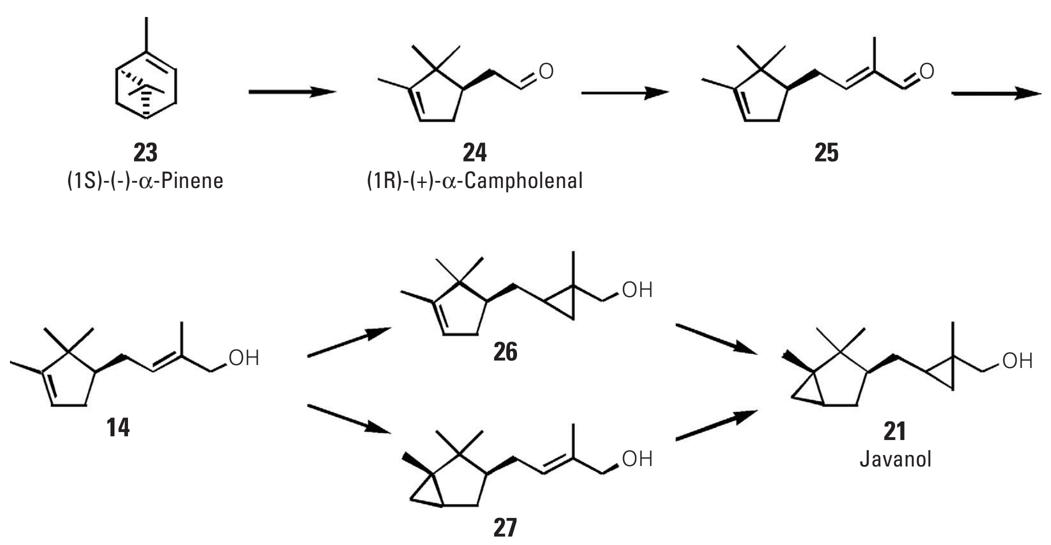
As the overall shape of such molecules depends heavily upon the structure of the flexible spacer, and because it can be assumed that the vicinity of the osmophore must be crucial for the odor, this spacer rapidly became the main object of Givaudan's structure-odor relationship sandalwood studies.[9] One of the modifications of this flexible fragment consisted of the introduction of a rigidifying and electron-rich cyclopropane ring. This appeared as a purely research option—no industrial-scale cyclopropanation process was reported; any development of such structures seemed highly improbable, but was attempted with reward.[9b,10] Most of the new compounds bearing a cyclopropane ring in the spacer exhibited interesting sandalwood-type olfactory profiles. The simultaneous introduction of a second three-membered ring into the bulky moiety proved even better. The best product obtained in the process later was called Javanol (**21**). This name was chosen to evoke the excellent quality of Java's sandalwood oil, which is, unfortunately, no longer available for perfumery creations. Javanol's olfactory profile and efficient performance across application platforms justified the difficult development of an industrially viable double-cyclopropanation process (F-3).

Javanol is prepared from turpentine obtained from pine trees. It is reassuring to realize that this common species is contributing to the protection of an endangered one (*S. album*). Moreover, using α-pinene (**23**), a natural, nonpetrol-derived starting material, to build the bulk of the Javanol structure (true for all the campholenal derivatives) contributes also to sustained development on our planet.

Javanol in Creation

In terms of chemistry, Javanol, with its two cyclopropane rings, is a rather unique fragrance ingredient. Its stability is greatly enhanced in all applications by the lack of double bonds in its structure (F-4). Its odor threshold is also the lowest among all the sandalwood-smelling odorants reported and more than 20 times lower than that of (Z)-(-)-β-santalol (**1**)—the main odor vector of natural sandalwood oil.

Preparation of Javanol **F-3**



Despite Javanol's relatively low volatility, its odor value (OV = vapor pressure divided by odor threshold)—a measure of airborne scent availability—is highest among the sandalwood odorants (F-5).

Its odor is close to that of β-santalol, with a dry woody, slightly vetiverlike nuance, and additional floral-rosy and creamy-musky facets. This complex and natural-seeming olfactory profile, combined with the physicochemical properties described previously, allow for versatile applications in fine fragrances, as well as in consumer products.

A Perfumer's Notes: Antoine Gaillard[b]

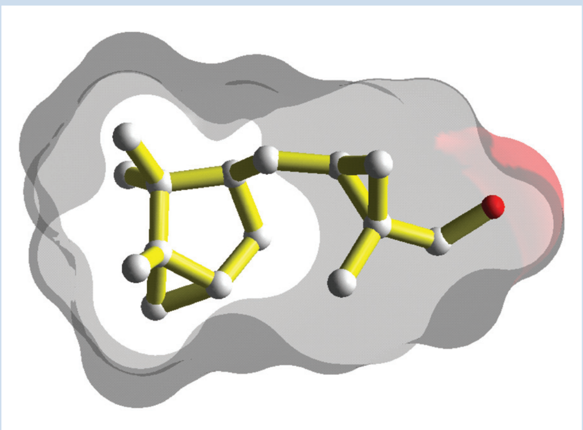
Challenges formulating sandalwood notes: The very specific scent of sandalwood oil is difficult to reproduce with a single molecule. The odor develops during evaporation of the oil and varies, depending upon the type of application in which it was incorporated. Consequently, a mixture of several synthetic sandalwood substitutes is necessary in order to obtain the olfactory profile of natural sandalwood oil. The composition of the mixture also has to be modified in respect to the performance needed.

Because of its performance and stability (F-5), Javanol can be used as the backbone for all modern sandalwood notes. Using it in combination with more diffusive and complementary molecules from the Polysantol and Ebanol families allows perfumers to reproduce a targeted olfactory effect. In some cases, a very small dosage of Javanol (0.02%) can produce a boosting effect, conferring additional volume and improved substantivity to more traditional sandalwood-type composition.

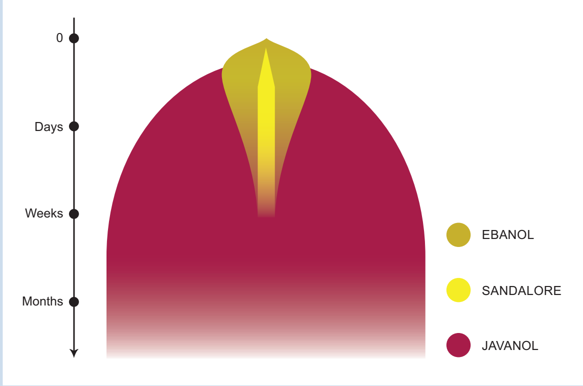
Javanol applications beyond sandalwood: Javanol is not exclusively a sandalwood note vector. Its additional olfactive facets and low threshold enable trace amounts of the substance to impart interesting volume and radiance effects to all types of perfumes. The material rounds and provides sophisticated density to musky, floral, spicy and woody accords.

[b]Antoine Gaillard is a senior perfumer with Givaudan.

Putative active conformation of Javanol with its solvent-accessible surface — F-4



Substantivity and volume/radiance of three different sandalwood odorants — F-5



Common applications: Because of its volume and extreme tenacity, Javanol can be used in all applications. When used in trace amounts, it proves efficient—even on dry fabrics and candles.

Application Example 1: In this demonstration, Javanol helps to soften a woody-ambery accord by adding a smooth, creamy and warm facet to accompany the inherent dryness of such materials.

Men's cologne at 6% alcohol 90° — T-1

Petitgrain oil (Paraguay)	5
Mandarin oil (Italy)	20
Bergamote Givco 104 (Givaudan)	170
Dihydromyrcenol	80
Ultrazur (Givaudan)	8
Black pepper oil	3
Cardamom seed oil	3
Eugenol	5
β-Damascone @ 1%	5
Geranium oil (Egypt)	10
Pharaone 10% (Givaudan)	3
Salvia officinalis (sage) oil	4
Juniper berry oil	4
Florhydral (Givaudan)	3
Lilial (Givaudan)	50
Hedione (Firmenich)	70
Indole @ 10%	5
β-Dihydro ionone	50
Oxyoctaline formate (Givaudan)	30
Vertofix (IFF)	50
Ambrofix (Givaudan)	6
Javanol (Givaudan)	3
Ambrettolide (IFF)	3
Velvione (Givaudan)	10
Galaxolide 50 (IFF)	100
Dipropylene glycol	300
TOTAL	**1,000**

Women's cologne at 12% alcohol 90°	T-2
Bergamot oil (Italy)	130
Pharaone 10% (Givaudan)	1
Styrallyl acetate	3
Toscanol (Givaudan)	2
Damascenone	1
Maltol crist.	3
Coumarin	15
β-Ionone	50
Isoraldeine 95 (Givaudan)	30
Hedione (Firmenich)	200
Lilial (Givaudan)	90
Heliotropine	20
Vanillin	10
Patchouli oil	8
Iso E Super IFF	35
Ebanol (Givaudan)	1
Javanol (Givaudan)	1
Velvione (Givaudan)	20
Tonalide	130
Galaxolide 50 (IFF)	250
TOTAL	**1,000**

Application Example 2: In chypres and in floral bouquets of a dominant jasmine or rosy type, a very small quantity of Javanol augments their richness, supporting both the middle and dry-down notes (T-2).

Application Example 3: In any accord, trace amounts (parts per 10,000) of Javanol added to musk help to reinforce its warmth and impart a "vibration" to the whole composition. In the case of a detergent fragrance, this trace is perceived integrally both on wet and dry fabrics (T-3).

Unusual/novel applications: We have employed sandalwood notes in air fresheners because now we have more economical performance/effects with the new generation of sandalwood chemicals. Due to its low threshold, Javanol is useful in trace amounts in consumer products. Because of Ebanol's good vapor pressure, it is suitable in air fresheners.

Sandalwood's growing popularity: The popularity of sandalwood notes in perfumes is growing due to several factors:

- Consumers are looking for more effective perfumes with more volume.
- "Cocoonlike" woody accords are increasingly popular.
- Gourmand and Oriental trends are more and more sought after.
- Sophisticated musky notes are in demand.

Environmental considerations: The latest generation of sandalwood materials provides an excellent alternative to increasingly rare and expensive natural oil. These materials enable today's perfumers to achieve the same effects while hopefully helping to decrease the overall demand (and illegal harvesting) of the threatened *S. album*. These new molecules also allow for the continued use of sandalwood notes in future creations.

Acknowledgments

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Perfume for laundry detergent at 0.3% — **T-3**

Ethyl methyl-2 butyrate	2
Manzanate	3
δ-Damascenone @ 10%	5
Verdox (IFF)	70
Allyl amyl glycolate	7
Dihydromyrcenol	100
Citronellyl nitrile	15
Aldehyde C 110 undecylic	4
Triplal (IFF)	4
Florhydral (Givaudan)	3
cis-3-Hexenol	1
Styrallyl acetate	4
Verdyl acetate	40
Tetrahydro linalool	80
Citronellol	60
Terpineol	60
Coumarin	5
Methyl Laitone 10% (Givaudan)	2
Neroline	40
Lilial (Givaudan)	50
Javanol @ 10% (Givaudan)	5
Cyclopentadecanolide	20
Iso E Super (IFF)	60
Peonile (Givaudan)	30
Hexyl cinnamic aldehyde	80
Dipropylene glycol	250
TOTAL	**1,000**

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